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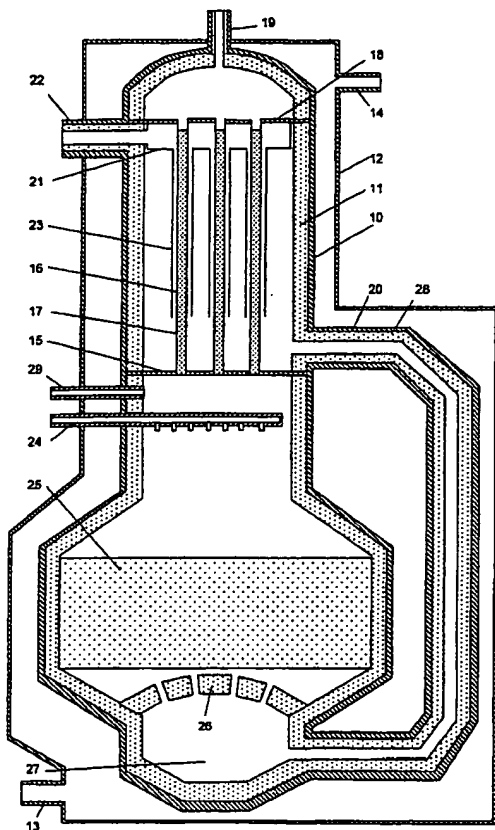
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(54) Title: STEAM REFORMER



(57) Abstract: Steam reforming apparatus having a primary reforming zone containing a plurality of primary reforming tubes (16) and means (20) to supply a hot fluid medium to the exterior of said tubes to heat said tubes and a secondary reforming zone (25) provided with means (24) to supply an oxygen-containing gas thereto, a combustion region and, optionally, a secondary reforming catalyst region. The primary and secondary reforming zones are located within a metal shell (10) provided on its interior surface with refractory insulation on its interior surface, is provided to transfer secondary reformed gas from said secondary reforming zone to said primary reforming zone for use as the hot fluid medium. The shell and conduit means are enclosed within a jacket (12) provided with means to supply a coolant thereto whereby the exterior surfaces of said shell and conduit are cooled by the coolant thereby reducing the thermal expansion to which the shell and conduit are subject during operation.

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STEAM REFORMER

This invention relates to steam reforming. Steam reforming is widely employed to produce hydrogen and synthesis gas, for example synthesis gas for the synthesis of ammonia or methanol or for Fischer Tropsch reactions, and involves passing a gaseous mixture
5 containing a hydrocarbon feedstock and steam and/or carbon dioxide at an elevated temperature and pressure through a steam reforming catalyst. As the steam reforming reaction is strongly endothermic, in the so-called primary reforming process, the catalyst, which is usually nickel, or sometimes ruthenium, on an oxidic support such as alumina, zirconia, or a calcium aluminate cement, is normally disposed in externally heated tubes. Typically the tubes
10 are heated such that the reformed gas leaves the catalyst at a temperature in the range 700 to 900°C. The reformed gas comprises hydrogen, carbon oxides, methane, steam and possibly inerts if such were present in the feedstock. The composition of the primary reformed gas depends on the composition of the gas mixture fed to the catalyst, the pressure, the temperature at which the reformed gas leaves the catalyst and how closely equilibrium is
15 approached. The latter in turn depends on the activity of the catalyst.

In some cases the primary reformed gas is subjected to a secondary reforming process wherein the primary reformed gas is subjected to partial combustion with an oxygen-containing gas, for example air, enriched air or substantially pure oxygen, and optionally then passed
20 through a secondary reforming catalyst, which again is typically nickel or ruthenium supported on an oxidic support as aforesaid. The partial combustion stage raises the temperature of the primary reformed gas mixture and further reforming takes place adiabatically. As a result of the partial combustion and further reforming, the resultant secondary reformed gas is normally at a temperature significantly greater than that of the primary reformed gas and has a methane content significantly lower than that of the primary reformed gas.

25 There have been various proposals, see for example US 4079017, GB 2181740, GB 2199841 and EP 0194067, to employ the hot secondary reformed gas as the medium used to heat the primary reforming catalyst, and indeed there have been proposals, e.g. in the aforesaid GB 2181740 and GB 2199841, to effect both the primary and secondary reforming processes within a single vessel. In the present invention both primary and secondary
30 reforming are effected in a single vessel using the secondary reformed gas to heat the catalyst-containing primary reformer tubes.

In the embodiment of the aforesaid GB 2181740 that employs a secondary reforming catalyst, the secondary reforming catalyst is disposed as a single bed round the exterior of the upper ends of the primary reforming tubes. As a result, over a relatively short portion of their
35 length, the primary reforming tubes are subjected to a large temperature differential, from the temperature of the partially combusted primary reformed gas at the outlet end of the primary reformer tubes, to the significantly lower temperature at which the secondary reformed gas leaves the bed of secondary reforming catalyst. This leads to metallurgical problems.

In the arrangement of GB 2199841, the secondary reforming catalyst is disposed as a bed around a central conduit which serves to transfer the primary reformed gas from the outlet of the primary reforming tubes through the secondary reforming bed to the partial combustion zone. Again this conduit is necessarily subjected to a large differential in temperature.

- 5 GB 2199841 also discloses that the apparatus may be of a double shell construction with a coolant flowing through the annular space, or jacket, between the inner and outer shells. A refractory material is provided between the inner shell and the primary and secondary reforming zones. This has the advantage that the temperature of the load-bearing inner shell can be kept substantially uniform with the large temperature gradients occurring across the refractory material which is only required to carry much lower mechanical loads. We have realised that this jacketed construction can advantageously also be applied to the conduit employed to transfer the secondary reformed gas back to the primary reforming zone for use as the heating gas therein.
- 10

- Accordingly the present invention provides steam reforming apparatus having a primary reforming zone containing a plurality of primary reforming tubes and means to supply a hot fluid medium to the exterior of said tubes to heat said tubes and a secondary reforming zone provided with means to supply an oxygen-containing gas thereto, a combustion region and, optionally, a secondary reforming catalyst region, said primary and secondary reforming zones being located within a metal shell provided on its interior surface with refractory insulation, said shell being enclosed within a first jacket provided with means to supply a coolant thereto whereby the exterior surface of said shell is cooled by said coolant, and wherein conduit means are provided to transfer secondary reformed gas from said secondary reforming zone to said primary reforming zone for use as the hot fluid medium, said conduit means comprising a metal conduit having refractory insulation on its interior surface and located within said first jacket, or within a second jacket in communication with said first jacket, whereby the exterior surface of said conduit is cooled by said coolant.
- 15
- 20
- 25

- As a result of enclosing the conduit within a jacket, which is the same as the jacket enclosing the reformer shell or is a jacket in communication with the jacket enclosing the reformer shell and through which the coolant supplied to the shell jacket also passes, the conduit is maintained at essentially the same temperature as the reformer shell. As a result, metallurgical problems are ameliorated. The coolant within the jacket, or jackets, is typically boiling water, which may be at an elevated pressure.
- 30

- In a preferred embodiment the primary reforming zone is provided with hot fluid medium off-take means and each primary reforming tube is provided with a sheath tube surrounding the reforming tube and extending from the hot fluid medium off-take means for a major portion of the length of said reforming tube whereby said sheath tubes to define a flow path for the hot fluid medium to flow past the exterior surfaces of the reforming tubes to the hot fluid medium off-take zone.
- 35

The refractory insulation may be any suitable material that can withstand large temperature gradients. Examples of such materials are fireclay, high temperature concrete, refractory oxides such as alumina and magnesia, for example such materials in a fibrous form.

The invention is illustrated by reference to the accompanying drawing which is a
5 diagrammatic section through apparatus in accordance with the invention.

The apparatus comprises a metal pressure shell 10, provided on its interior surface with a layer 11 of a refractory insulation material. The shell 10 is supported, by means not shown, inside a jacket 12 provided with coolant inlet and outlet conduits 13, 14.

The shell is divided by a tube plate 15 into an upper primary reforming section and a
10 lower secondary reforming section. In the upper primary reforming section, a plurality of primary reforming tubes 16 containing a primary steam reforming catalyst 17 are disposed. Only three tubes are shown: in practice there may be 10's or 100's of such tubes. These tubes depend from an upper tube sheet 18 or other suitable supporting means. The shell 10 is provided at its upper end with an inlet conduit 19 extending through the jacket 12 for supplying
15 a feedstock/steam mixture to the upper ends of the primary reforming tubes 16.

At the lower end of the primary reforming zone, the shell 10 is provided with a conduit 20 for supplying a heating medium to the exterior surfaces of the reforming tubes 16. Supported by the tube plate 18 is a product gas off-take can 21 connected to a product outlet conduit 22 extending through the shell 10 and jacket 12. Depending from can 21 are a plurality of sheath
20 tubes 23, one associated with, and surrounding each, reforming tube 16. The sheath tubes 23 extend for a major proportion of the length of the reforming tubes 16 and serve to define a narrow flow path for the heating medium supplied via conduit 20, past the exterior surfaces of tubes 16, and into the product gas off-take can 21.

Reforming tubes 16 are open at their lower ends and extend through tube plate 15 and
25 are free to expand longitudinally to accommodate thermal expansion. A suitable seal may be provided between tubes 16 and plate 15 to permit sliding movement. The seal arrangement described in US 5958364 is particularly suitable.

In the lower secondary reforming zone, a conduit 24 is disposed for the supply of an oxygen-containing gas, and beneath this conduit is a bed 25 of a secondary reforming catalyst.
30 This is supported over a perforated refractory arch 26 at the lower end of the shell 10 by means of an inert particulate material (not shown). Conduit 20 communicates with the space 27 below arch 26. Conduit 20, like shell 10, has a lining of refractory insulation 28 and is disposed within the jacket 12 so that the exterior of the conduit 20 is cooled by the coolant in jacket 12.

In use the feedstock/steam mixture supplied to inlet conduit 19 is primary reformed in
35 tubes 16 and the resultant primary reformed gas then passes from the open lower ends of tubes 16 into the secondary reforming zone. Here it is partially combusted with the oxygen-containing gas supplied via conduit 24 and then undergoes further reforming adiabatically in catalyst bed 25. The resultant hot secondary reformed gas then passes into space 27 and then

through conduit 20 back into the primary reforming zone as the heating medium used therein to heat the primary reforming tubes 16. The secondary reformed gas passes up the annulus between the interior of the sheath tubes 23 and the exterior surface of the primary reforming tube 16 associated with the sheath tube, and so heats the primary reforming tubes 16 and supplies the heat required for the primary reforming reaction. As it passes up the annulus, the secondary reformed gas cools and then passes into can 21 and leaves the shell via product gas off-take conduit 22.

In a preferred embodiment, a further conduit 29 is provided through the jacket 12 and shell 10. This conduit may be used to supply a hot combustible gas at start-up of the apparatus, for example as described in US 4788004, US 4938685 and US 5110563, and/or to supply a further amount of the feedstock/steam mixture and/or to supply a further amount of primary reformed gas from another primary reformer, for example one heated by combustion of a fuel.

In a typical example, the feedstock/steam mixture is supplied to conduit 19 at a temperature of 450°C, and undergoes primary reforming in tubes 16 leaving tubes 16 at 700°C. Upon partial combustion with oxygen fed at 200°C through conduit 24, the primary reformed gas is heated to about 1200°C and then undergoes adiabatic secondary reforming in bed 25, cooling to 1000°C. The secondary reformed gas then passes through conduit 20 and heats the tubes 16, entering the off-take can 21 at 600°C. Boiler feed water below 100°C is fed into the jacket 12 by means of conduit 13. The water within jacket 12 is heated by heat losses through refractory insulation 11, 28 until it reaches its boiling point. Steam created by this boiling is vented to atmosphere from the jacket via conduit 14, which is sized sufficiently large so as to impose a negligible back pressure within the jacket 12. The water within jacket 12 is therefore essentially at atmospheric pressure and so boils at 100°C. It is seen that there are considerable temperature differences between the components, but the shell 10 and conduit 20 are both maintained at a substantially constant temperature, approximately 100°C, by means of the coolant in jacket 12. The temperature gradients are thus largely across the refractory insulation 11, 28. Consequently the amount of thermal expansion of the shell 10 is relatively small. Although shell 10 is a pressure vessel, since it is maintained at a relatively low temperature by the coolant in the jacket 12, it can be constructed from a thinner gauge material than would be the case if the cooling jacket were to be omitted. Since both the shell 10 and the conduit 20 are at substantially the same temperature, there will be relatively little difference in the expanded lengths of the metal and so there is no requirement to construct conduit 20 from long lengths of pipe with large expansion loops and conduit 20 can take a direct route from space 27 to the exterior of reforming tubes 16, thereby minimising cost and heat losses.

Reforming tubes 16 are of course subject to high temperatures and a significant temperature gradient will exist along their length. Upon passage through the tubes 16, through bed 25 and through conduit 20, the process gas will undergo some pressure drop. However

this will normally be not more than a few bar. Hence, since the pressure inside the tubes 16 will be not more than a few bar above that of the secondary reformed gas used to heat the tubes, relatively light gauge material may be employed. As indicated above, thermal expansion of the tubes 16 can be accommodated by allowing them to slide through tube plate 15. Sheath
5 tubes 23 and products off-take can 21 will also be subject to temperature gradients and subject to thermal expansion but again they are relatively lightly loaded mechanically and so can also be made of relatively light gauge material.

Claims

1. Steam reforming apparatus having a primary reforming zone containing a plurality of primary reforming tubes and means to supply a hot fluid medium to the exterior of said tubes to heat said tubes and a secondary reforming zone provided with means to supply an oxygen-containing gas thereto, a combustion region and, optionally, a secondary reforming catalyst region, said primary and secondary reforming zones being located within a metal shell provided on its interior surface with refractory insulation, said shell being enclosed within a first jacket provided with means to supply a coolant thereto whereby the exterior surface of said shell is cooled by said coolant, and wherein conduit means are provided to transfer secondary reformed gas from said secondary reforming zone to said primary reforming zone for use as the hot fluid medium, said conduit means comprising a metal conduit having refractory insulation on its interior surface and located within said first jacket, or within a second jacket in communication with said first jacket, whereby the exterior surface of said conduit is cooled by said coolant.
2. Steam reforming apparatus as claimed in claim 1 wherein the primary reforming zone is separated from the secondary reforming zone by a tube plate through which the primary reforming tubes slidably extend.
3. Steam reforming apparatus according to claim 1 or claim 2 wherein the primary reforming zone is provided with hot fluid medium off-take means and each primary reforming tube is provided with a sheath tube surrounding the reforming tube and extending from the hot fluid medium off-take means for a major portion of the length of said reforming tube whereby said sheath tubes to define a flow path for the hot fluid medium to flow past the exterior surfaces of the reforming tubes to the hot fluid medium off-take zone.

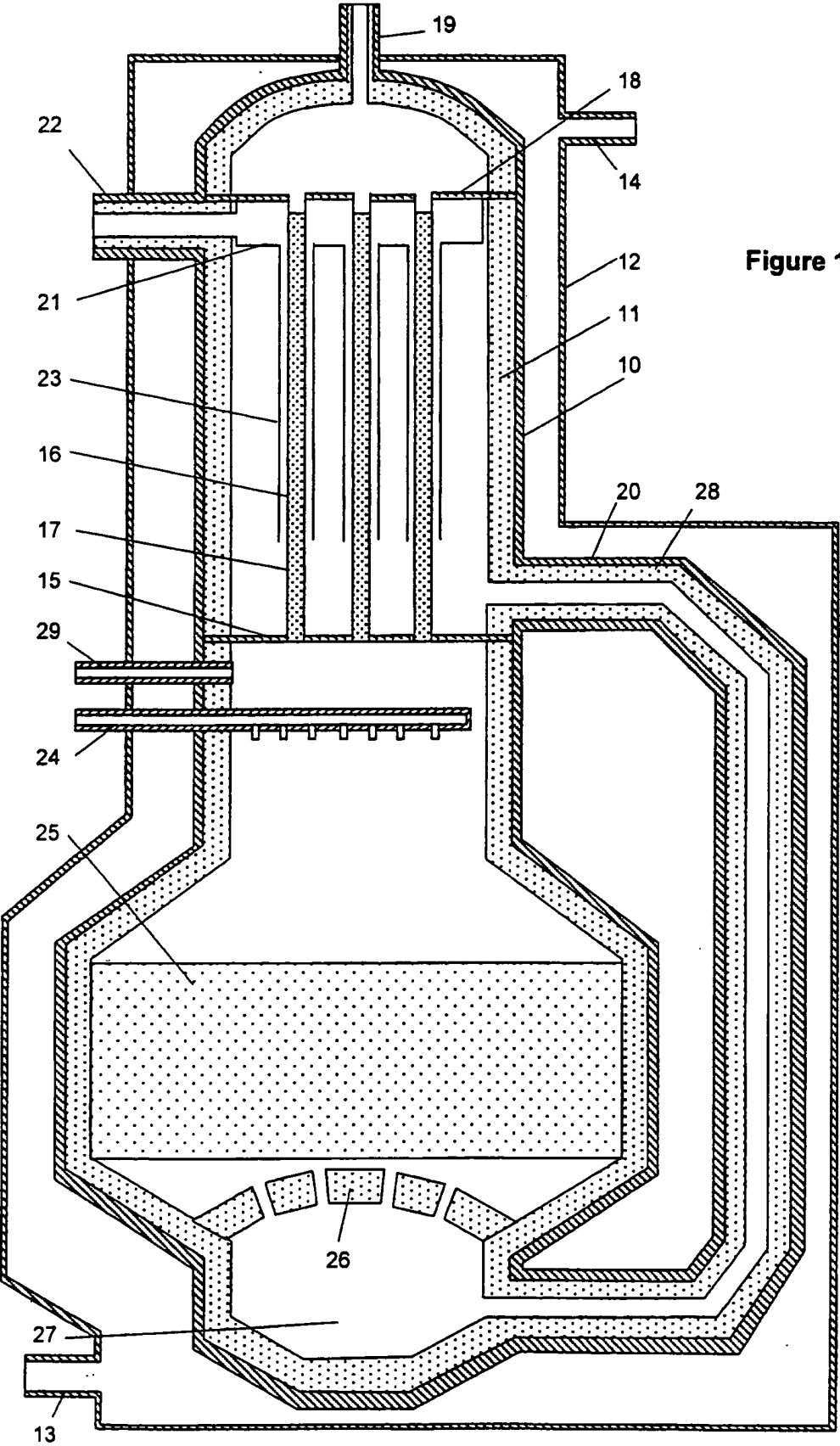


Figure 1

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B3/38 B01J8/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 199 841 A (UNION CARBIDE CORP) 20 July 1988 (1988-07-20) cited in the application claims 1,23-39; figure page 17, line 18 - line 27	1-3
A	US 5 958 364 A (DUNNE MICHAEL DAVID ET AL) 28 September 1999 (1999-09-28) cited in the application column 4, line 18 - line 28 claims; figures	1-3
A	GB 2 181 740 A (UHDE GMBH) 29 April 1987 (1987-04-29) cited in the application claims; figures	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/00024

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 222 533 A (HUMPHREYS & GLASGOW LTD) 14 March 1990 (1990-03-14) the whole document ---	1
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